

Final Report for AOARD Grant FA2386-10-1-4047
Development and Characterization of New Donor-Acceptor Conjugated Polymers and Fullerene Nanoparticles for High Performance Bulk Heterojunction Solar Cells

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Abstract:

We have prepared a bithiophene/thieno[3,4-*c*]pyrrole-4,6-dione (TPD)-based donor-acceptor polymer, **PBTPD**, that exhibits high crystallinity and a low-lying highest occupied molecular orbital. An optimal device incorporating a **PBTPD**/[6,6]-phenyl-C₆₁-butyric acid methyl ester blend (1:1.5, w/w) displayed an open circuit voltage of 0.95 V and a power conversion efficiency of 4.7%.

A novel molecular design concept was introduced to develop a series of new conjugated polymers with donor- π -bridge-acceptor side chains for high efficiency polymer solar cells. Different from the commonly used linear D-A conjugated polymers, the acceptor of the polymers are located at the end of the side chains and connected with the electron-rich unit on the main chain through a π -bridge. This method provides a facile way to tune the bandgaps and energy levels of the polymers by simply varying the acceptors on the side chains. A systematic study was performed in this project to elucidate the relationship among molecular structure-morphology-device properties to explore the full potential of applying these new materials for OPV applications.

Introduction:

The development of small band gap conjugated polymers as efficient electron donors is one of the most challenging topics for achieving high performance OPVs. Among many materials that have been explored as donor, poly(3-hexylthiophene) (P3HT), shows promising performance with PCE of ~ 5%. However, it is difficult to further improve the efficiency of P3HT-based OPVs due to the mismatched absorption with the solar spectrum and the relatively small energy offset between its highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of fullerene derivatives which limits the magnitude of the short circuit current and open circuit voltage. To optimize the material properties, conjugated polymers with alternating electron-rich and electron-deficient unit along their backbone have been extensively studied because their absorption spectra and band gaps can be tuned easily by controlling intramolecular charge transfer (ICT) between the donor and acceptor. Using this approach, several narrow band gap donor-acceptor type (D-A) conjugated polymers have shown promising performances with PCE as high as ~7.5%. However, in these linear D-A polymers, the molecular interactions and packing orientation of the conjugating

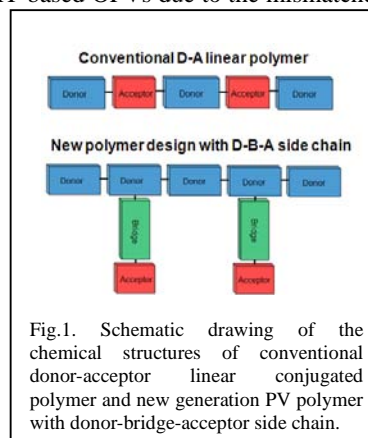


Fig.1. Schematic drawing of the chemical structures of conventional donor-acceptor linear conjugated polymer and new generation PV polymer with donor-bridge-acceptor side chain.

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14. ABSTRACT Bithiophene/thieno[3,4-c]pyrrole-4,6-dione (TPD)?based donor?acceptor polymer, PBTTTPD, that exhibits high crystallinity and a low-lying highest occupied molecular orbital was prepared. A device incorporating a PBTTTPD/[6,6]-phenyl-C61-butyric acid methyl ester blend (1:1.5, w/w) displayed an open circuit voltage of 0.95 V and a power conversion efficiency of 4.7%. A molecular design concept was introduced to develop a series of new conjugated polymers with donor-?-bridge-acceptor side chains for high-efficiency polymer solar cells. Different from the commonly used linear D-A conjugated polymers, the acceptor of the polymers are located at the end of the side chains and connected with the electron-rich unit on the main chain through a ?-bridge. This method provides a facile way to tune the bandgaps and energy levels of the polymers by simply varying the acceptors on the side chains. A systematic study was performed in this project to elucidate the relationship among molecular structure-morphology-device properties to explore the full potential of applying these new materials for OPV applications.					
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moieties need to be carefully controlled to ensure proper processability and charge-transporting properties.

To provide a simple and generally applicable method for improving the properties of active materials, we had synthesized a series of new conjugated polymers with D- π -bridge-A side chains for high efficiency OPVs. Different from the commonly used linear D-A conjugated polymers, the acceptor of the proposed polymers are located at the end of the side chains and connected with the electron-rich unit on the main chain through a π -bridge (Fig. 1). This method provides a facile way to tune the bandgap and energy level of the polymers by simply varying the acceptors on the side chains. In addition, the exciton dissociation ability can also be improved as the generated excitons can be readily dissociated into electrons and holes due to the internal field produced by the dipole moment built on the D-A molecular structures followed by subsequent charge transfer to the nearby fullerene acceptors.

The electron-deficient thieno[3,4-*c*]pyrrole-4,6-dione (TPD) moiety exhibits a symmetric, rigidly fused, coplanar structure and strong electron-withdrawing properties, which make it a potential system for increasing intramolecular/ intermolecular interactions, reducing optical bandgaps, and/or lowering highest occupied molecular orbital (HOMO) energy levels when incorporated into polymeric backbones. Several p-type conjugated polymers containing the symmetric bi(dodecyl)thiophene unit exhibit crystalline characteristics and high hole mobilities when used in organic field effect transistors.

Considering not only the electronic energy level but also the hole mobility, we prepared a new D-A polymer, **PBTPD**, wherein the electron-withdrawing TPD unit was conjugated with the symmetrical electron-donating bi(dodecyl)thiophene unit to provide crystalline characteristics and a low-lying HOMO energy level. Because of these desirable features, we expected **PBTPD** to exhibit good hole mobility and high values of open-circuit voltage (V_{oc}) when used in photovoltaic applications.

Experiment:

Detail experimental: ^1H and ^{13}C NMR spectra were measured using a Bruker 500 instrument spectrometer operating respectively at 125 MHz for ^{13}C and 500 MHz for ^1H in deuterated chloroform solution with TMS internal standard as a reference for chemical shifts. Molecular weights of the polymers were determined by a Waters 1515 gel permeation chromatograph (GPC) with a refractive index detector in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. UV-Vis spectra were obtained on a Perkin-Elmer Lambda-9 spectrophotometer. Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) using a DSC2010 with a heating rate of $10^\circ\text{C}/\text{min}$. Cyclic voltametric data were measured on a BAS CV-50W voltametric analyzer using tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile (electrochemical grade, Fisher Scientific) as electrolyte and indium tin oxide (ITO) and Ag/Ag^+ as the working and reference electrode at a scan rate of 100 mV/s at room temperature under argon, respectively. The highest occupied molecular orbital (HOMO) energy level of polymers are calculated by using ferrocene value of -4.8 eV below the vacuum level as the internal standard. The lowest unoccupied molecular orbital (LUMO) were estimated from their optical band gap and HOMO energy. Atomic force microscope (AFM) images were obtained using a Veeco multimode AFM with a Nanoscope III controller under tapping mode.

Top contact organic FETs were fabricated on heavily n-doped silicon substrates with a 300 nm thick thermally grown SiO_2 dielectric. Before organic semiconductor deposition, the substrates were treated with hexamethyldisilazane (HMDS) by vapor phase deposition in a vacuum oven. The organic semiconductor films were spin-coated at in a dry nitrogen environment from a 5 mg mL^{-1} chloroform solution. Interdigitated source and drain electrodes were defined by evaporating a 50 nm thick gold film through a shadow mask from a resistively heated Mo boat. FETs characterization was carried out in air using the Agilent 4155B semiconductor parameter analyzer. The field-effect mobility was calculated in the saturated regime from derivative plots of the square root of the source-drain current versus gate voltage.

To fabricate polymer solar cell devices, ITO-coated glass substrates were cleaned with solvents followed by an oxygen plasma treatment. A thin layer (ca. 40 nm) of PEDOT:PSS (Baytron P VP AI 4083, filtered at 0.45 μm) was first spin-coated on the pre-cleaned ITO-coated glass substrates at 5,000 rpm and baked at 140°C for 10 minutes under ambient condition. The substrates were then transferred into an argon-filled glove-box. Subsequently, the polymer:PCBM active layer (ca. 80 nm) was spin-coated on the PEDOT:PSS layer at 1,000 rpm from a homogeneously blended solution. The solution was prepared by dissolving the polymer (5 mg mL^{-1}) and PC_{71}BM (20 mg mL^{-1}) in

1,2-dichlorobenzene and filtered with a 0.2 μm PTFE filter. The substrates were annealed at 150 $^{\circ}\text{C}$ for 10 minutes prior to electrode deposition. At the final stage, the substrates were pumped down to high vacuum ($< 2 \times 10^{-6}$ Torr), and calcium (10 nm) topped with aluminum (100 nm) was thermally evaporated onto the active layer through shadow masks to define the active area of the devices. The current density-voltage (J - V) characteristics of photovoltaic devices were measured under ambient using a Keithley 2400 source-measurement unit. An Oriel xenon lamp (450 W) with an AM 1.5 G filter was used as the solar simulator. The light intensity was calibrated to 100 mW cm^{-2} using a calibrated silicon cell with KG5 filter, which is traced to the National Renewable Energy Laboratory. External quantum efficiency (EQE) measurements were taken using a monochromator (Newport, Cornerstone 130) joined to the same xenon lamp and a lock-in amplifier (Stanford Research Systems, SR 830) coupled to a light chopper.

We prepared **PBTTPD** through Stille polymerization of the monomers 1,3-dibromo-5-ethyl-hexylthieno[3,4-*c*]pyrrole-4,6-dione and 4,4'-didocecyl-5,5'-bis(trimethylstannyl)-2,2'-bithiophene using $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tolyl})_3$ as the catalyst. The molecular weight and purity of the polymer was determined by GPC and ^1H NMR analysis, respectively. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-Vis spectroscopic analysis, cyclic voltammetry (CV), and X-ray diffraction (XRD) measurements were performed to analyze the properties of the polymer. Topography and phase images of the polymer blends were obtained using a Digital Nanoscope III atomic force microscope (AFM). The thickness of active layer was measured using a Veeco Dektak 150 surface profiler. Hole mobility and photovoltaic properties measurements were performed using the devices fabricated with the structures of ITO/PEDOT:PSS/**PBTTPD** blend/Au and ITO/PEDOT:PSS/**PBTTPD**:PCBM/Al, respectively.

A new series of new conjugated polymers were synthesized. The physical and chemical properties of the polymers were characterized using a combination of measurements including NMR, GPC, DSC, cyclic voltammetry and UV-vis absorption. The film formation property and morphology of the polymer films were studied using atomic force microscopy. The electrical properties of the polymers were studied in thin film transistors and their charge carrier mobilities were measured. Finally the polymers were tested in bulk-heterojunction devices and the photovoltaic properties were optimized.

Results and Discussion:

A new class of conjugated polymers was developed based on the modifications of the abovementioned D-A side-chain conjugated copolymers. The chemical structures of some of the polymers are shown in Figure 2a. This new design takes advantage of the in-depth knowledge that has been accumulated for developing high performance nonlinear optical chromophores and will use it to guide synthesis of polymers with optimized absorption and energy levels. In our earlier work, the fluorene-triarylamine main chain has the similar structure as that of the literature reported polymer with high mobility of holes ($0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). In addition, the two-dimensional conjugated structure of these polymers was designed to improve their isotropic charge transport, which is important for OPVs. The optical band gap of PF-DCN was calculated from the onset of the film absorption to be 1.87 eV. By using stronger acceptors, such as PF-PDT and PF-DCNIO, the derived polymers exhibit significantly red-shifted intramolecular charge transfer peak compared to that of PF-DCN, corresponding to a smaller optical bandgap of 1.76 eV and 1.55 eV, respectively (Figure 2b). The HOMO energy level of PF-DCN, PF-PDT and PF-DCNIO are calculated to be -5.30, -5.26 and -5.25, respectively based on the cyclic voltammetry studies. As a result, the corresponding LUMO of polymers are -3.43, -3.50 and -3.70 eV based on the estimation from the difference between the optical band gaps and HOMO energy levels.

All these polymers exhibit similar HOMO energy levels due to the same donor main chain, while their LUMO energy levels could be systematically tuned by adjusting the acceptors on the side chains. Preliminary OPV study on these materials show an encouraging PCE as high as 4.8% and an open circuit voltage of 1 V (Figure 2c). Theoretical calculation of the optimal performance of these polymers based on the energy levels and bandgaps indicated that their PCEs should be able to reach ~9-10%. The possible reason for the lower PCE obtained is that the non-planar structure of the triarylamine donor prevents polymer chains from packing tightly. As a result, it causes severe PCBM intercalation (1:4 ratio instead of the 1:1 for P3HT). This dilutes the concentration of the light absorbing material to only 20% in the active layer. If a fused ring, more planar aromatic donors with low-lying HOMO can be used, both the light harvesting and charge transporting properties of these

polymers can be significantly improved. A factor of two of improvement should be achievable if the concentration of the active polymer can be increased from 20% to 40%.

To overcome this deficiency, we next generation side-chain polymers should be based on more planar aromatic donors with low-lying HOMO to improve the molecular packing, light harvesting and charge transporting properties of these polymers. We suggest to replace the non-planar triphenylamine donor with several new planar donors with tunable donating properties. Some possible new donor units includes fused triarylamine or fused carbazol. All these planar donors can effectively improve the planarity of the polymer backbone, which is critical to improve the molecular packing of the polymers and eventually leads to polymers that have better PV performance.

The number-average molecular weight (M_n) of **PBTPD** was 9.7 kg mol^{-1} , with a polydispersity of

1.4. **PBTPD** reveals an excellent thermal stability with a decomposition temperature (T_d) greater than 400°C ; that exhibits a melting point at 297°C and a crystallization point at 268°C . **PBTPD** features high crystallinity and order structure by the XRD measurement; that exhibits a maximum absorption at 572 nm , with a pronounced vibronic shoulder at 628 nm , implying its ordered arrangement in the solid film and strong π - π stacking between polymer chains. The presence of the electron-deficient TPD moiety in the polymer chain provided **PBTPD** with a lower optical bandgap relative to P3HT and a low-lying HOMO energy level of 5.56 eV . The hole mobility of the pristine **PBTPD** and **PBTPD**:PCBM (1:1.5, w/w) film was $1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $8 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, as determined using the space-charge-limited current (SCLC) method, presumably because its crystalline characteristics promoted charge transport in the device. An optimal performance was obtained from the device with an active layer that comprised a blend of **PBTPD** and PCBM at a weight ratio of 1:1.5; this device displayed a value of V_{oc} of 0.95 V , a short-circuit current density (J_{sc}) of 8.02 mA cm^{-2} , a fill factor of 0.62, and a resulting power conversion efficiency (PCE) of 4.7%, indicating that **PBTPD** has a great promise for solar cell applications. Further to optimize the composition and morphology of the polymer blend through the employment of PC₇₀BM and solvent additives, we believe the PCEs of devices based on this polymer can be significantly enhanced in our further work.

List of Publications:

1. Mao-Chuan Yuan, Mao-Yuan Chiu, Shih-Pin Liu, Chia-Min Chen, and Kung-Hwa Wei* "A Thieno[3,4-c]pyrrole-4,6-dione-Based Donor-Acceptor Polymer Exhibiting High Crystallinity for Photovoltaic Applications" *Macromolecules*, 2010, 43, 6936.
2. Duan, C.; Chen, K.-S.; Huang, F.; Yip, H.-L.; Liu, S.; Zhang, J.; Jen, A. K.-Y.; Cao, Y. "Synthesis, Characterization, and Photovoltaic Properties of Carbazole-Based Two-Dimensional Conjugated Polymers with Donor- π -Bridge-Acceptor Side Chains" *Chemistry of Materials*, 2010, 22, 6444.

